

REMARKS

By this Preliminary Amendment, the Specification has been amended to include a cross-reference to related applications which has been inserted in page 1. Also pages 1, 5, and 10 have been amended to recite the Specification section headings required by U.S. practice. In addition, pages 4 and 5 of the U.S. Specification have been amended to conform to the changes made in the International Office.

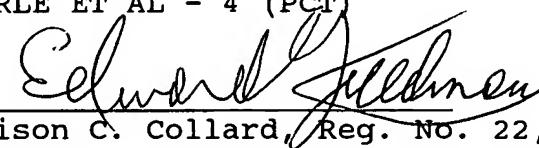
The amendments to the claims are to cancel the originally filed claims 1 to 22 without prejudice, and to replace these claims with new claims 23 to 43. New claims 23 to 43 eliminate the multiple dependency of the claims, so as to avoid the U.S.P.T.O. surcharge therefor. Also claims 23 to 43 have been written so as to comply with U.S. formal requirements. Claims 23 to 43 correspond to the amended claims filed in the International Office.

An Abstract of the Disclosure on its own separate page is enclosed.

No new matter has been introduced by this amendment. Entry of this amendment is respectfully requested.

Respectfully submitted,

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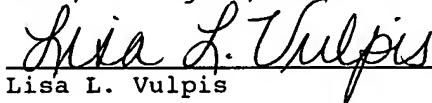
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Enclosure: (1) Abstract of the Disclosure;  
(2) Marked-Up Version of Amended Specification pages  
1, 4, 5 and 10;

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I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10, on the date indicated above, and is addressed to the U.S. Patent and Trademark Office, Box PCT, P.O. Box 2327, Arlington, VA 22202.

  
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531 Rec. CT/PT 03 JAN 2002

MARKED-UP VERSION  
OF  
AMENDED SPECIFICATION

531 Rec'd 03 JAN 2002

Process for producing monolithic oxidation catalysts and their use in the gas-phase oxidation of hydrocarbons

CROSS REFERENCE TO RELATED APPLICATIONS

BACKGROUND OF THE INVENTION

5 1. Field of the Invention The invention relates to a process for producing monolithic oxidation catalysts and to their  
7 use in the gas-phase oxidation of hydrocarbons.

8 2. The Prior Art Supported catalysts for the gas-phase oxidation 10 products such as carboxylic acids, carboxylic anhydrides or aldehydes, which catalysts have a catalytically active surface coating consisting essentially of titanium dioxide ( $TiO_2$ ) and divanadium pentoxide ( $V_2O_5$ ), have been known for a long time. A 15 typical example of the use of such catalysts is the preparation of phthalic anhydride, in which mixtures of o-xylene and air or naphthalene and air or o-xylene, naphthalene and air are passed over an appropriate catalyst in a shell-and-tube reactor. The heat 20 generated in this strongly exothermic reaction is customarily removed (cooling, isothermal reaction conditions) by means of a salt melt which surrounds the reaction tubes.

The supported catalysts used here comprise an 25 inert support body, for example having a ring shape or a spherical shape, on which the actual catalytically active composition is present. The active composition consists predominantly of the main components  $TiO_2$  in the anatase form and  $V_2O_5$ . To improve the control of the 30 activity and to improve the selectivity, further activating or deactivating additives, for example oxides of transition elements or alkali metal compounds, are frequently added in small amounts as dopants (promoters) to the catalytically active 35 composition.

The supported catalysts are generally produced by spraying aqueous suspensions or aqueous solutions of  $TiO_2$  and  $V_2O_5$ , frequently with addition of promoters and

downstream adiabatic reactor. This process variant is likewise intended to enable the phthalic anhydride formed to be obtained largely free of by-products and without a loss in yield. Here too, a shaft oven is 5 claimed as adiabatic reactor.

6 AT-A 9201926 describes a process for preparing phthalic anhydride in a main reactor having a downstream adiabatic reaction zone. Here, it is expressly stated that, for economic reasons, it is 10 advantageous for the adiabatic reactor to be connected directly to the main reactor. Apart from the use of catalyst base bodies in the form of rings or spheres, mention is also made of the possible use of a catalyst having a monolithic structure, for example in the form 15 of a honeycomb. In the reaction procedure described, this measure enables the yield of phthalic anhydride to be increased by about 1% by weight. The formation of the by-product phthalide is at the same time significantly reduced. The use of the monolithic 20 catalyst shape mentioned is not described in any example. Likewise, no details are given of the production of a monolithic catalyst and associated 25 problems.

23 Owing to the laminar flow occurring in honeycomb catalysts, they have only a very low pressure drop even at very high gas velocities. However, a disadvantage is that, owing to the lack of turbulent flow resulting from the shape, heat and mass transfer in the honeycomb channels, and thus heat removal, are 30 greatly reduced. This situation makes use of honeycomb catalysts as catalyst supports virtually impossible for strongly exothermic processes in conjunction with a selective oxidation. Honeycomb catalysts have therefore become established industrially only in waste gas 35 purification or waste gas incineration where all the organic constituents undergo total oxidation to CO<sub>2</sub>.

Coating monolithic support material with a catalytically active composition comprising the main

constituents  $TiO_2$ ,  $V_2O_5$  and possibly dopants by generally known methods, for example a dipping process, is found to be impractical. This is because coating suspensions based on commercially available  $TiO_2$  have a 5 very high viscosity even at solids concentrations of 30-35% by weight and thus make coating of the channels of a monolithic support material virtually impossible without blocking the channels.

In order to coat monolithic catalyst supports 10 with the necessary amount of catalytically active composition, for example 50-150 g of active composition per liter of catalyst, the coating process would have to be carried out with such a low-concentration "active composition" suspension that the necessary layer 15 thickness would be achieved only after repeating the coating process a number of times. However, this at the same time once again increases the problem of blocking of the channels in the catalyst support because of the multiple coating steps. Furthermore, this is associated 20 with significantly more work and thus with increased 21 costs and is therefore uneconomical.

22 ~~summary of the invention~~  
It is therefore an object of the invention to provide a simple and preferably single-stage process for producing monolithic catalysts based on  $TiO_2$ /metal 25 oxides.

It has now surprisingly been found that the viscosity of highly concentrated  $TiO_2$  coating suspensions having a high solids content can be greatly reduced by addition of surfactants.

30 The invention provides a process for producing monolithic supported catalysts for gas-phase oxidation by coating the catalyst support by means of a suspension, wherein the latter comprises catalytically active composition <sup>and</sup> comprising one or more types of  $TiO_2$ , 35 and 1-10% by weight of one or more surfactants of the formula



The monolithic catalysts produced according to the invention are particularly suitable for preparing phthalic anhydride in an adiabatic reactor (after-reactor) in combination with an isothermally operated 5 reactor (main reactor, for example filled with a bed of particulate catalyst).

10 The adiabatic reactor can also be operated advantageously with upstream gas cooling. In a particularly preferred embodiment, the upstream gas cooling and the adiabatic reaction are carried out in a joint apparatus.

15 In industry, it is customary to cool the reaction gas in a gas cooler before isolation of the product. The upstream gas cooling, the adiabatic reaction in the monolithic catalyst bed and further cooling can be carried out within the reactor or outside the reactor,

17 or in a joint apparatus.

18 DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS  
The invention is illustrated in more detail by the following examples.

20 The following examples demonstrate the influence of surfactants from the group consisting of phosphoric esters on the viscosity of support oxide suspensions. The flow behavior of the suspensions prepared was determined by a method based on DIN 53211 25 using a flow cup. Two types of  $TiO_2$  which differed from one another only in the particle size were tested. The mean particle diameter was 0.1 and 0.4  $\mu m$ , respectively. This measurement method was selected since it could appropriately simulate flow of a suspension out 30 of the honeycomb channels. As outflow nozzle, use was made of a nozzle having a diameter of 2 mm corresponding to a flow orifice area of  $3.14 \text{ mm}^2$ . For comparison, a 200 csi honeycomb has a channel cross section of  $2.3 \text{ mm}^2$  and a 100 csi honeycomb has a 35 channel cross section of  $4.66 \text{ mm}^2$ . If the viscosity of the suspension was too high, i.e. the suspension could not flow through the nozzle under these conditions, the experiment was repeated using a nozzle opening of 4 mm